Electronic Structure and Rydberg-Core Interactions in Hydroxycarbene and Methylhydroxycarbene

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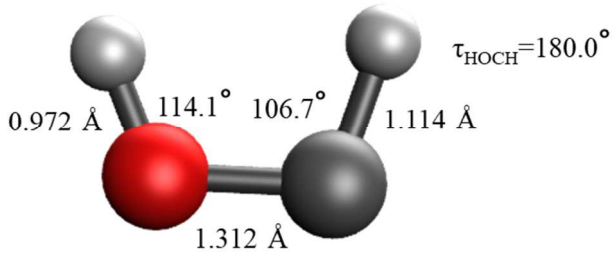
Supplemental Information

I. Structures

All the results are in good agreement with previously reported results.[1-5]

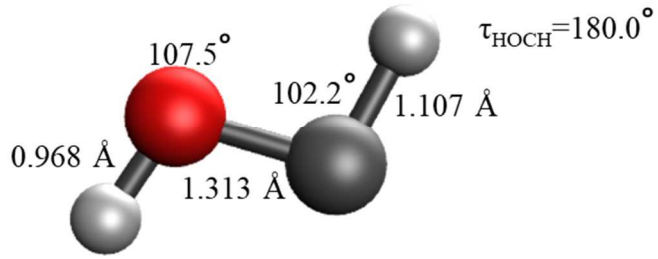
a. Hydroxycarbene (HC)

S_0 geometry of *cis*-hydroxycarbene optimized at the MP2/aug-cc-pVTZ level



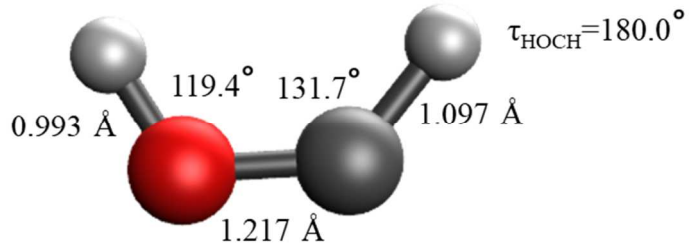

```
H       0.9316120240    -0.8075743777     0.0000000000
O       0.5741481585     0.0970737059    -0.0000000000
C      -0.7368118639     0.1546627254    -0.0000000000
H      -1.1039261084    -0.8969916220     0.0000000000
Nuclear Repulsion Energy =   30.638201
MP2 energy               = -114.220014
```

S_0 geometry of *trans*-hydroxycarbene optimized at the MP2/aug-cc-pVTZ level



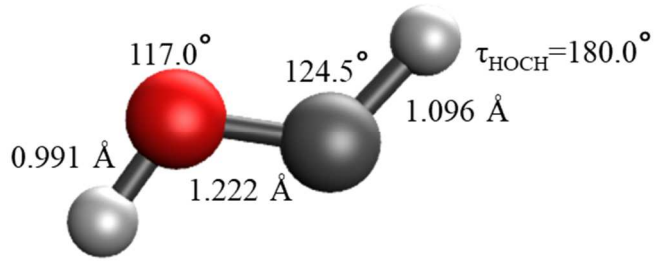

```
H       1.0946972316    -0.6448108655    -0.0000000000
O       0.5495211998     0.1552848846     0.0000000000
C      -0.7077398040    -0.2236842521    -0.0000000000
H      -1.2444280064     0.7446373011     0.0000000000
Nuclear Repulsion Energy =   30.735659
MP2 energy               = -114.228119
```

D_0 geometry of *cis*-hydroxycarbene cation optimized at the MP2/aug-cc-pVTZ level



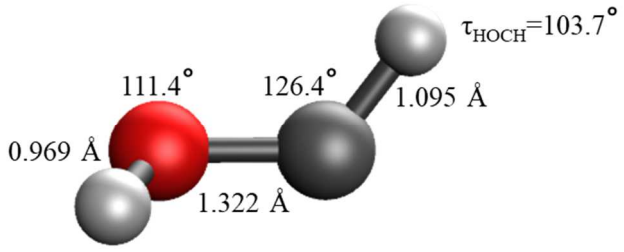

```
H       -1.0911149057    -0.7511035811     0.0000000000
O       -0.5545062056     0.0844539309     0.0000000000
C        0.6605549330     0.0150990918     0.0000000000
H        1.3430928313    -0.8436456674     0.0000000000
Nuclear Repulsion Energy =   31.910311
MP2 energy               = -113.900137
```

D_0 geometry of *trans*-hydroxycarbene cation optimized at the MP2/aug-cc-pVTZ level



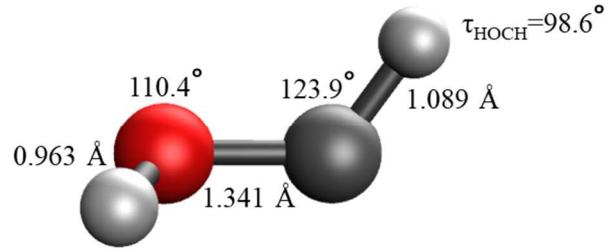

```
H        1.1457613514    -0.7051695695     0.0000000000
O        0.5690470822     0.1011885423     0.0000000000
C       -0.6396763487    -0.0803383286     0.0000000000
H       -1.3877214100     0.7202321970     0.0000000000
Nuclear Repulsion Energy =   31.872637
MP2 energy               = -113.906021
```

S_1 geometry of hydroxycarbene optimized at the EOM-EE-CCSD/aug-cc-pVTZ level




```
H        1.0607771681     0.6860769042    -0.2594430355
O        0.5810032732    -0.0718121667     0.1078402207
C       -0.7115247527    -0.0008460332    -0.1607811870
H       -1.5056601577     0.2874068822     0.5354763693
Nuclear Repulsion Energy =   30.303616
S1 CCSD total energy     = -114.154259
```

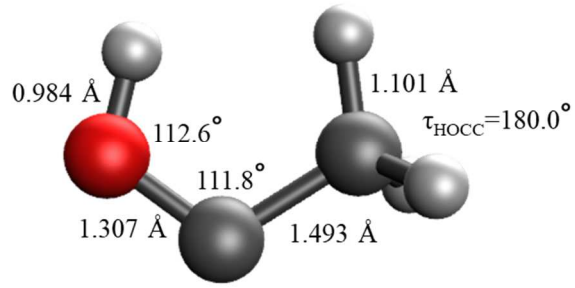
T_1 geometry of hydroxycarbene optimized at the EOM-EE-CCSD/aug-cc-pVTZ level




```
H       1.0378363542     0.6974439577    -0.2444137309
O       0.5882009344    -0.0798388592     0.1044610699
C      -0.7226165780    -0.0258055921    -0.1724375227
H      -1.4788251797     0.3090260801     0.5354825511
Nuclear Repulsion Energy =   30.092369
T1 CCSD total energy     = -114.205276
```

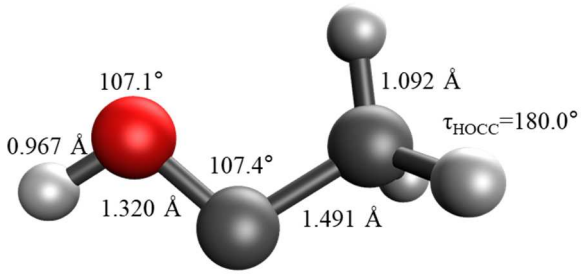
b. **Methylhydroxycarbene (MHC)**

S_0 geometry of *cis*-methylhydroxycarbene optimized at the MP2/aug-cc-pVTZ level



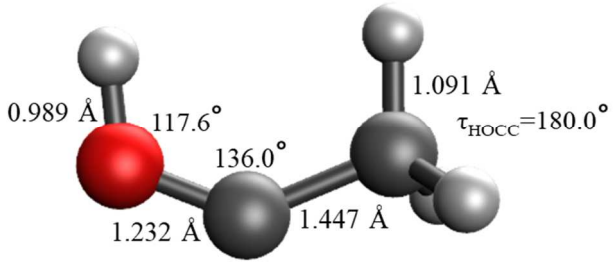

```
O       1.1868344540     0.1237451207    -0.0000000000
H       0.9564841243     1.0802177211    -0.0000000000
C       0.1311852606    -0.6462793952     0.0000000000
C      -1.1343508851     0.1462742942    -0.0000000000
H      -1.7177732417    -0.1544954477     0.8716029000
H      -1.7177732417    -0.1544954477    -0.8716029000
H      -0.9966195255     1.2388428153    -0.0000000000
Nuclear Repulsion Energy =   69.672121
MP2 energy               = -153.462104
```

S_0 geometry of *trans*-methylhydroxycarbene optimized at the MP2/aug-cc-pVTZ level



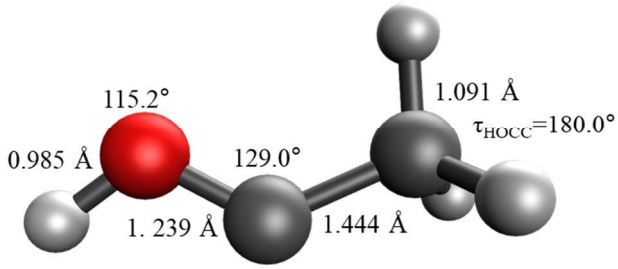
```
C       1.1574204338     0.1371534061    -0.0000000000
O      -1.0964950192     0.2778337929    -0.0000000000
H       1.7253406425    -0.1978982463     0.8645856348
H       1.0584925919     1.2202974024    -0.0000000000
H       1.7253406425    -0.1978982463    -0.8645856348
C      -0.1260902644    -0.6090798883     0.0000000000
H      -1.9251947395    -0.2156123598     0.0000000000
Nuclear Repulsion Energy =   69.770894
MP2 energy               = -153.468105
```

D_0 geometry of *cis*-methylhydroxycarbene cation optimized at the MP2/aug-cc-pVTZ level



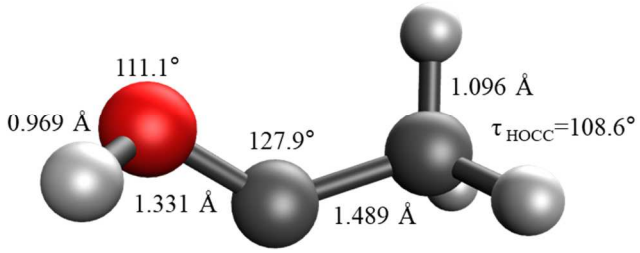

```
O       1.2442734591     0.0538163374     0.0000000000
H       1.3512202539     1.0373724474     0.0000000000
C       0.0971118289    -0.3955794103     0.0000000000
C      -1.2385297899     0.1610514884     0.0000000000
H      -1.7577765415    -0.2376069072     0.8769859738
H      -1.7577765415    -0.2376069072    -0.8769859738
H      -1.2305357242     1.2523626121     0.0000000000
Nuclear Repulsion Energy =   70.040142
MP2 energy               = -153.165275
```

D_0 geometry of *trans*-methylhydroxycarbene cation optimized at the MP2/aug-cc-pVTZ level



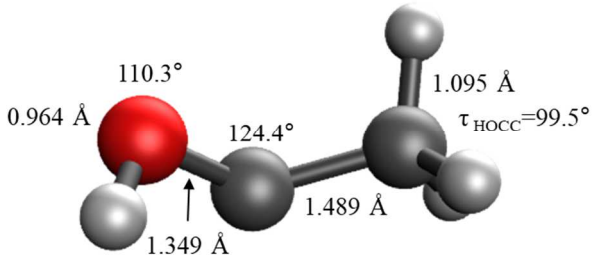

```
C       1.2272647677     0.1147545737    -0.0143911962
O      -1.1956380277     0.0975723190    -0.0625750253
H       1.7430401758    -0.2435518156     0.8816480176
H       1.1765686242     1.2033889786    -0.0499703210
H       1.7699120156    -0.2982983222    -0.8704671172
C      -0.0937864517    -0.4675695343    -0.0184102140
H      -1.9761801169    -0.5039153508    -0.0561023428
Nuclear Repulsion Energy =   70.100590
MP2 energy               = -153.171879
```

S_1 geometry of methylhydroxycarbene optimized at the EOM-EE-CCSD/aug-cc-pVTZ level




```
C       -0.1199435478    -0.3855470494    -0.0716671909
O       -1.2575253575     0.3042131902    -0.0410852365
H       -1.7084351335     0.1974482805     0.8102310123
C        1.2716697780     0.1429915721    -0.0414360962
H        1.9186349669    -0.4544178957    -0.6827316237
H        1.7055698473     0.1344466800     0.9689033581
H        1.2618230596     1.1750262329    -0.4095116992
Nuclear Repulsion Energy =   67.657603
S1 CCSD total energy     = -153.394659
```

T_1 geometry of methylhydroxycarbene optimized at the EOM-EE-CCSD/aug-cc-pVTZ level




```
C       -0.0931884049    -0.5103692318     0.0262351846
O       -1.2564854601     0.1583647597    -0.1170889652
H       -1.6597206035     0.3153306331     0.7438577867
C        1.2519732928     0.1267875746     0.0009698765
H        2.0218102457    -0.6393114675     0.0781668010
H        1.3809680152     0.8281948100     0.8332018243
H        1.4029682448     0.6756365454    -0.9342127736
Nuclear Repulsion Energy =   67.590893
T1 CCSD total energy     = -153.446982
```

II. Singlet-Triplet Gaps

Table S1: Comparison of S-T gap energy (in kcal/mol) calculated in this work at the EOM-EE-CCSD/aug-cc-pVTZ basis set with previously reported values.[1,2,5]

$\Delta E_{S-T}^{adiabatic}$(kcal/mol)	This work	Schreiner *et al.*[a]	Matus *et al.*[b]
HC	24.61	27.97	25.3
MHC	29.20	30.64	30.5

[a]calculated using (aug)-cc-p(C)VXZ basis sets with coupled-cluster theory, incorporating triple excitation and higher-order correlation effects at the CCSDT(Q) level.
[b]thermochemical calculation at CCSD(T)/aug-cc-pVnZ level of theory where n = D, T, Q, and 5, extrapolated to the complete basis set limit.

III. Orbital Orientations in S_1

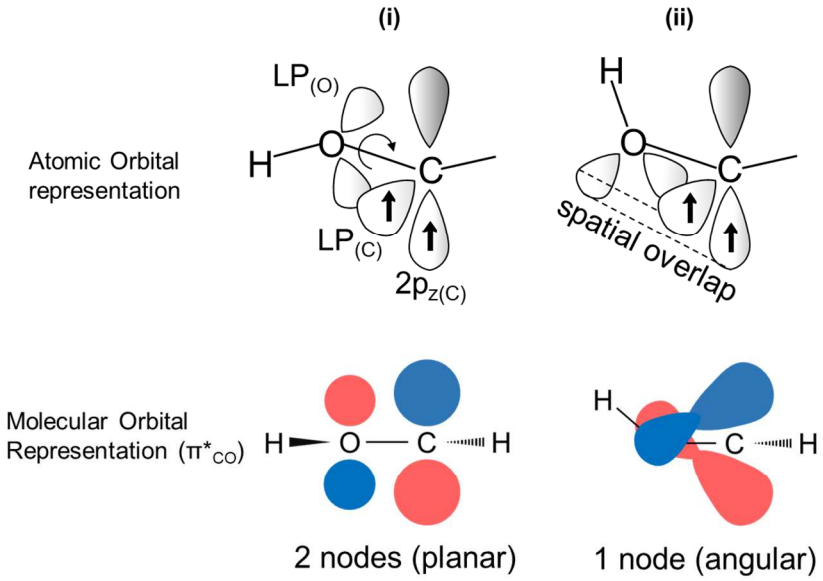


Figure S1: Representation of the orbitals at (i) planar and (ii) twisted geometries in the first excited state of HC. The top row represents the stabilization of the singly occupied electron deficient C orbitals by the O lone pairs. This stabilization can also be explained by using a molecular orbital picture (bottom row), which demonstrates the change in the nodal planes upon rotation about the CO bond.

IV. EOM-EE Results

Table S2: Vertical singlet excitation energy computed with EOM-EE-CCSD/aug-cc-pVTZ. Five A' states (white) and five A" states (gray) are calculated.

a. **HC**

	cis-HC			*trans*-HC		
States	Energy (eV)	Oscillator Strength	Type of Excitation	Energy (eV)	Oscillator Strength	Type of Excitation
2^1A'	5.34	0.025	3s←n (Ryd)	5.67	0.010	3s←n (Ryd)
3^1A'	6.77	0.065	3p←n (Ryd)	6.65	0.036	3p←n (Ryd)
4^1A'	7.65	0.057		7.51	0.089	
5^1A'	8.14	0.026	3d←n (Ryd)	8.23	0.033	3d←n (Ryd)
6^1A'	8.63	0.023		8.86	0.008	
1^1A"	3.08	0.010	π*←n (Val)	3.05	0.009	π*←n (Val)
2^1A"	7.54	0.013	3p←n (Ryd)	7.54	0.026	3p←n (Ryd)
3^1A"	8.09	0.007	π*←$lp_{(O)}$ (Val)	9.57	0.007	π*←$lp_{(O)}$ (Val)
4^1A"	9.81	0.002	3d←n (Ryd)	9.80	0.001	3d←n (Ryd)
5^1A"	10.08	0.005	3s← π (Ryd)	10.25	0.015	

b. **MHC**

	cis-MHC			*trans*-MHC		
States	Energy	Oscillator Strength	Type of Excitation	Energy	Oscillator Strength	Type of Excitation
2^1A'	5.59	0.062	3s←n (Ryd)	5.47	0.007	3s←n (Ryd)
3^1A'	6.42	0.065	3p←n (Ryd)	6.37	0.023	3p←n (Ryd)
4^1A'	6.74	0.124		6.79	0.137	
5^1A'	7.61	0.001	3d←n (Ryd)	7.57	0.021	3d←n (Ryd)
6^1A'	7.68	0.024		7.67	0.008	
1^1A"	3.49	0.011	π*←n (Val)	3.40	0.010	π*←n (Val)
2^1A"	6.75	0.042	3p←n (Ryd)	6.72	0.047	3p←n (Ryd)
3^1A"	7.93	0.006	3d←n (Ryd)	7.90	0.008	3d←n (Ryd)
4^1A"	8.00	0.009	π*←$lp_{(O)}$ (Val)	8.34	0.004	
5^1A"	8.12	0.004	3d←n (Ryd)	9.06	0.011	π*←$lp_{(O)}$ (Val)

V. NTOs

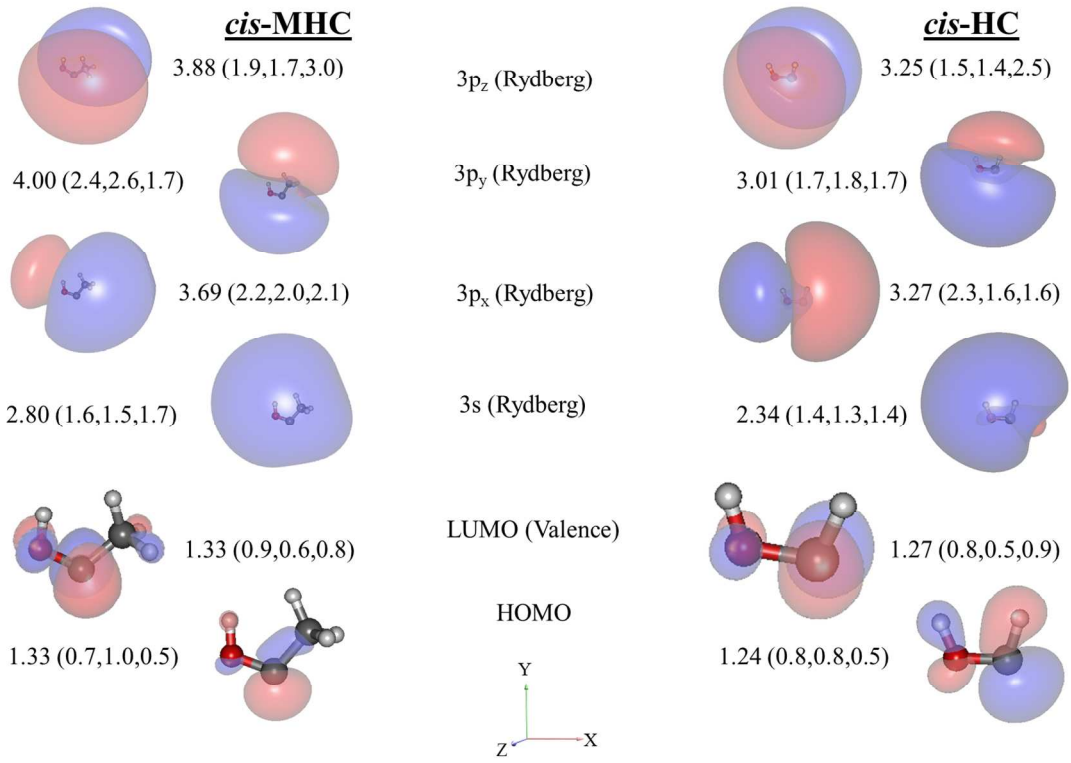


Figure S2: Particle NTOs, and the hole NTO (labeled HOMO) for the lowest excited states of *cis*-MHC (left) and *cis*-HC (right); their directional spatial extents in Å are labeled as $\langle r \rangle$ ($\langle r_x \rangle$,$\langle r_y \rangle$,$\langle r_z \rangle$); The orientation of the molecules has been kept the same in all pictures.

VI. References

1. Schreiner, P. R.; Reisenauer, H. P.; Pickard IV, F. C.; Simmonett, A. C.; Allen, W. D.; Mátyus, E.; Császár, A. G., Capture of hydroxymethylene and its fast disappearance through tunnelling. *Nature* **2008**, *453*, 906-911.
2. Schreiner, P. R.; Reisenauer, H. P.; Ley, D.; Gerbig, D.; Wu, C.-H.; Allen, W. D., Methylhydroxycarbene: Tunneling Control of a Chemical Reaction. *Science* **2011**, *332*, 1300-1303.
3. Koziol, L.; Wang, Y.; Braams, B. J.; Bowman, J. M.; Krylov, A. I., The Theoretical Prediction of Infrared Spectra of *trans*-and *cis*-Hydroxycarbene Calculated Using Full Dimensional Ab Initio Potential Energy and Dipole Moment Surfaces. *J. Chem. Phys.* **2008**, *128*, 204310.
4. Koziol, L.; Mozhayskiy, V. A.; Braams, B. J.; Bowman, J. M.; Krylov, A. I., Ab Initio Calculation of the Photoelectron Spectra of the Hydroxycarbene Diradicals. *J. Phys. Chem. A* **2009**, *113*, 7802-7809.
5. Matus, M. H.; Nguyen, M. T.; Dixon, D. A., Heats of Formation and Singlet− Triplet Separations of Hydroxymethylene and 1-Hydroxyethylidene. *J. Phys. Chem. A* **2006**, *110*, 8864-8871.